

PATENT ABSTRACTS OF JAPAN

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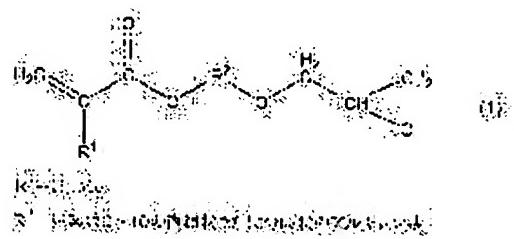
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(54) PHOTORESISTIVE RESIN COMPOSITION AND METHOD FOR FORMING AQUEOUS GEL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photosensitive resin composition obtained by using a poly(meth)acrylic acid, having excellent preservation stability, having compatibility and miscibility with, and solubility in various compound, and capable of being immobilized by light in high sensitivity even in a water-retaining condition; and to provide a method for forming an aqueous gel by using the composition.

SOLUTION: The photosensitive resin composition contains (A) a poly(meth)acrylic acid-based water-soluble photosensitive resin obtained by adding a compound represented by general formula (1) to a part of carboxy groups in a (meth)acrylic acid-based polymer, and having ≥ 150 mgKOH/g acid value of a solid component, (B) a photopolymerization initiator and (C) water.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]****[Field of the Invention]**

This invention relates to the formation approach of water gel of having used the photopolymer constituent of a photopolymerization mold, and it.

[0002]**[Description of the Prior Art]**

Since the Pori (meta) acrylic acid and its alkali neutralization object have the good physiological active substance and miscibility of hydrophilic properties, such as various drug effect components and enzymes, they are maintenance of these matter, and the purpose of immobilization, and are applied to waste water treatment, the base material of a diagnostic drug and a HAPPU agent, etc. These many are hardened by crosslinking reaction with the condition that the base material contained water, and are used as the so-called water gel which performs maintenance of the quality of the specified substance, and immobilization. The operation of the water in this water gel has important duties, such as not only the dissolution of the matter in the film but emission speed control to the exterior or matter diffusion rate control from the outside.

[0003]

Conventionally, the heat-curing reaction has been used in water gel formation of the Pori (meta) acrylic acid and its alkali neutralization object. However, when the matter and volatile matter unstable with heat were fixed in gel, the reaction needed to be advanced at low temperature, and if long duration was not applied very much, there was a problem of several days that gel formation and immobilization did not fully advance (for example, patent reference 1 reference).

[0004]

In recent years, in these fields, the approach using the photo-setting resin as an outstanding method of fixing physiological active substances, such as an unstable enzyme, or a fungus body by un-heating with heat is recognized (for example, the patent reference 2 and 3 and 4 reference).

[0005]

however, by the so-called PVA-SbQ resin, among the photopolymers illustrated by these reference Since in addition to there being a physiological active substance, an enzyme, and a fault to which the range of the compound in which the mixed dissolution is possible is limited in immobilization of a fungus body since it has the part of the structure top cationicity of a compound sensibility falls extremely where many water is included, Sufficient hardenability was not acquired to fix the compound into which a desiccation process cannot be put with a moisture state, but there was a problem which runs short of the reinforcement of gel.

[0006]

In the case of the polymerization setup-of-tooling product using a cellulose system polymer, in order for sensibility to be unable to say that it is enough but to acquire required hardenability as a matter of fact, addition of a polymerization nature monomer is indispensable. It is substantially impossible to make this

polymerization nature monomer polymer-ize completely in a photo-curing reaction, and in order that the unreacted monomer which remained may cause problems, such as enzyme activity inhibition and a skin stimulus, it is difficult to actually apply to the purpose of enzyme immobilization or a HAPPU agent.

[0007]

The attempt which gives the bridge formation part of polymerization nature to the Pori (meta) acrylic acid is known from before using acrylic ester with an epoxy group (meta) (for example, patent reference 5 reference). However, in these reference, there is no publication about the constituent containing a photoresist and water, and it cannot apply to the water gel formation application which artificers make the purpose.

[0008]

Although some attempts which introduce a bridge formation radical into the Pori (meta) acrylic-acid system copolymer are reported using the acrylic ester which has an epoxy group similarly (meta) (the patent reference 6, 7 reference) All are aimed at application to a photoresist although these have a photoresist. Water solubility does not have sufficient water solubility in the neutral range depending on pH from the aescence, and artificers do not have sufficient physical properties in compatibility with various compounds, and the water content of gel on the occasion of the water gel formation made into the purpose.

[0009]

[Patent reference 1] JP,05-320612,A (paragraph [0013] - [0017] etc.)

[Patent reference 2] JP,8-23545,B (the 2nd page etc.)

[Patent reference 3] JP,2-240555,A (the 2nd page)

[Patent reference 4] JP,2-308805,A (the 3rd page etc.)

[Patent reference 5] JP,49-98878,A (the 3rd page etc.)

[Patent reference 6] JP,10-3167,A (paragraph [0005] - [0010] etc.)

[Patent reference 7] JP,4-337087,A (paragraph [0007] - [0010] etc.)

[Patent reference 8] JP,11-327139,A (paragraph [0005] - [0016] etc.)

[Patent reference 9] JP,2001-58972,A (paragraph [0005] - [0025] etc.)

[0010]

[Problem(s) to be Solved by the Invention]

Although it is a compound with the Pori (meta) acrylic acid important in order to form water gel in a HAPPU agent, a diagnostic drug, waste water treatment, etc. and the photo-curing method is effective in these applications as stated so far, a practical thing is not seen at all by the technique of having combined this.

[0011]

This invention makes it a technical problem to excel in preservation stability, and to have the compatibility over various compounds, and mixed solubility in view of such a situation, using the Pori (meta) acrylic acid, and to offer the formation approach of the water gel using the photopolymer constituent and it in which optical immobilization is possible also in a moisture state by high sensitivity.

[0012]

In addition, what introduced the alkylene group as a spacer between the epoxy group and the acrylic radical is reported in recent years as the cross-linking polymer compounded using acrylic ester with an epoxy group, and oligomer (for example, the patent reference 8, 9 reference). in addition to the improvement in physical physical properties of increase, improvement in a reaction rate, the toughness grant to a hardened material, etc., these have the degree of freedom of an acrylic (meta) radical advantageous also to safeties, such as toxicity and a stimulative fall, by the spacer effectiveness of an alkylene group -- it excels. However, the water gel formation which there is no description about the constituent which contains water solubility or water also in these reference, and water solubility is not accepted in a written example, and is made into artificers' purpose was impossible.

[0013]

[Means for Solving the Problem]

In order that this invention persons may solve the above-mentioned technical problem, as a result of

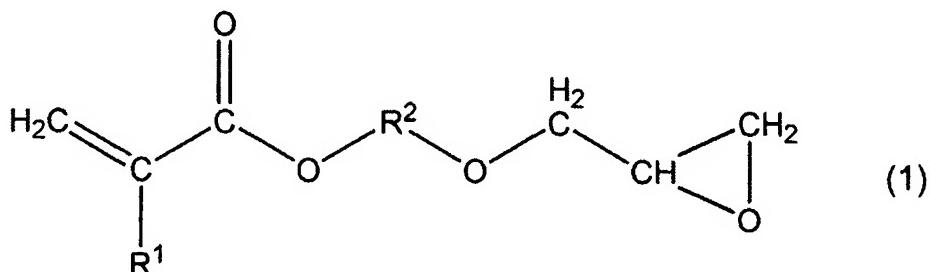
repeating examination wholeheartedly, a part of carboxyl group in an acrylic-acid (meta) system polymer By using the Pori (meta) acrylic-acid system water solubility photopolymer obtained by the addition reaction with the compound shown in the following general formula (1) It excels in the preservation stability using the Pori (meta) acrylic acid, and has the compatibility over various compounds, and mixed solubility, and came to complete the water gel formation approach using the photopolymer constituent and it in which optical immobilization is possible also in the moisture state by high sensitivity. In addition, in this specification, "an acrylic acid (meta)" means "an acrylic acid or a methacrylic acid."

[0014]

The 1st mode of this this invention is in the Pori (meta) acrylic-acid system water solubility photopolymer (A) which made the compound shown in the following general formula (1) add to a part of carboxyl group in an acrylic-acid (meta) system polymer and whose solid content acid number is 150 or more mgKOH/g, and a photopolymerization initiator (B) and the photopolymer constituent characterized by containing water (C).

[0015]

[Formula 2]



R¹ = H, Me

R² = 炭素数2～10の直鎖状または分岐状のアルキレン基

[0016]

The 2nd mode of this invention is in the photopolymer constituent characterized by neutralizing with alkali a part or all of a carboxyl group that the compound shown by said general formula (1) of the aforementioned (meta) acrylic-acid system polymer has not added in the 1st mode.

[0017]

The 3rd mode of this invention is in the formation approach of the water gel characterized by obtaining water gel by carrying out a photopolymerization reaction using the photopolymer constituent of the mode of the 1st or 2.

[0018]

The photopolymer constituent of this invention contains the Pori (meta) acrylic-acid system water solubility photopolymer (A), and a photopolymerization initiator (B) and water (C).

[0019]

A photopolymer (A) is obtained by carrying out epoxy ring breakage addition of the compound shown in the above-mentioned general formula (1) at a part of carboxyl group in an acrylic-acid (meta) system polymer.

[0020]

As a compound shown in this general formula (1), 2-hydroxyethyl AKURIRETOGURISHIJIRU ether, the 2-hydroxyethyl meta-KURIRETOGURISHIJIRU ether, 2-hydroxypropyl AKURIRETOGURISHIJIRU ether, 2-hydroxypropyl methacrylate glycidyl ether, 4-hydroxy butyl acrylate glycidyl ether, 4-hydroxy butyl methacrylate glycidyl ether, etc. can be mentioned, for example.

[0021]

Moreover, that in which the acrylic-acid (meta) homopolymer also copolymerized two or more sorts chosen from an acrylic-acid (meta) monomer, other vinyl monomers, and (meta) an acrylate monomer is sufficient as an acrylic-acid (meta) system polymer, and what performed side-chain denaturation of those other than the compound of a general formula (1) for them further is sufficient as it. Anyway, after an addition reaction with the compound shown in a general formula (1), 150 or more mgKOH/g of solid content acid numbers, it must be chosen so that it may become 170 or more mgKOH/g preferably.

[0022]

Although especially a limit does not have the molecular weight of a photopolymer (A), the range of 5000-2 million has desirable weight average molecular weight. It is because it will become hyperviscosity very much and handling will become difficult on the occasion of composition and spreading of a constituent, if sufficient hardenability may not be acquired and 2 million is exceeded less than in 5000.

[0023]

Although the rate of addition of the compound of a general formula (1) should be determined by the crosslinking density of the hardened material made into the purpose, and the mechanical strength and there is especially no limitation, 150 or more mgKOH/g of solid content acid numbers of the photopolymer after addition (A) must be 170 or more mgKOH/g preferably. When the solid content acid number is less than 150 mgKOH/g, it is because sufficient water solubility is not acquired.

[0024]

(Meta) The reaction which is made to add the compound shown in a general formula (1) to a part of carboxyl group in an acrylic-acid system polymer, and obtains a photopolymer (A) is usually performed by heat, the catalyst, or its concomitant use in a solution. Although especially a limit does not have the solvent which constitutes a solution, the presentation which the acrylic-acid system polymer to be used (meta) dissolves is desirable. As an example, water, a methanol, ethanol, IPA, n-butanol, A sec-butanol, isobutanol, a tert-butanol, ethylene glycol, Ethylene glycol, such as a diethylene glycol, triethylene glycol, and tetraethylene glycol Ethylene glycol monomethyl ether, the diethylene-glycol monomethyl ether, Glycol ether, such as ethylene glycol diethylether and diethylene-glycol wood ether Ethylene glycol monoethyl ether acetate, diethylene glycol monoethyl ether acetate, Glycol ether acetate, such as diethylene glycol monobutyl ether acetate Propylene glycols, such as propylene glycol, dipropylene glycol, and tripropylene glycol Propylene glycol monomethyl ether, the propylene glycol monoethyl ether, Dipropylene glycol monomethyl ether, the dipropylene glycol monoethyl ether, Propylene glycol wood ether, dipropylene glycol wood ether, Propylene glycol ether, such as propylene glycol diethylether and dipropylene glycol diethylether Propylene-glycol-monomethyl-ether acetate, propylene glycol monoethyl ether acetate, Propylene glycol ether acetate, such as dipropylene-glycol-monomethyl-ether acetate and dipropylene glycol monoethyl ether acetate Dimethyl sulfoxide, N-methyl pyrrolidone, dimethylformamide, dimethylacetamides, and those mixture are mentioned.

[0025]

Although there is no limit in the catalyst used for a reaction, by the acid catalyst, organic sulfonic acids, such as inorganic acids, such as a sulfuric acid, a phosphoric acid, and perchloric acid, Lewis acid of BF₃ grade, methansulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, and dodecylbenzenesulfonic acid, are mentioned as an example. As a basic catalyst, phosphorus compounds, such as quarternary ammonium salt, such as tertiary amine, such as triethylamine, tetramethylethylenediamine, tributylamine, a tree n-octyl amine, dimethyl benzylamine, and a pyridine, tetramethyl ammoniumchloride, tetramethylammonium bromide, tetraethylammonium bromide, and tetrabutylammonium bromide, triphenyl phosphine, and tributyl phosphine, are mentioned.

[0026]

Although there is no limit special to reaction temperature, the range of 120 degrees C is usually suitably used from a room temperature.

[0027]

When it constitutes the photopolymer constituent of this invention from a photopolymer compounded using solvents other than water, it is good to even dilute only with water, but it does not matter even if it supplies to nonpolar solvents, such as an aqueous solution or aliphatic hydrocarbon, aromatic hydrocarbon, ethyl acetate, and butyl acetate, after the solvent permutation by distilling out, or desiccation solidification and makes water remelt solid content after deposit separation.

[0028]

In addition, the carboxyl group which remains in a photopolymer (A) may be neutralized by the alkali compound also with the acid type. Although there is especially no limit in this alkali compound, if an example is given, inorganic alkali, such as a lithium, sodium, and a potassium, ammonia, the alkylamine of the 1-3rd class, the 4th class ammonium compound, etc. are applicable. Moreover, what is necessary is just to adjust suitably so that there may be no limit in whenever [neutralization] and it may be set to pH according to the purpose of use.

[0029]

The photopolymer constituent of this invention has an indispensable photopolymerization initiator. Moreover, in addition to a photopolymerization initiator, a photosensitizer may be added. It may be made to dissolve or distribute in a constituent, or a photopolymerization initiator may be chemically combined to a photopolymer. Although there is especially no limit in the photopolymerization initiator and photosensitizer which are applied, as an example Benzophenone, hydroxy benzophenone, screw-N, and N-dimethylamino benzophenone, Benzophenones, such as screw-N and N-diethylamino benzophenone and a 4-methoxy-4'-dimethylamino benzophenone A thioxan ton, 2, 4-diethylthio xanthone, an isopropyl thioxan ton, Thioxan tons, such as a chloro thioxan ton and an isopropoxy chloro thioxan ton Ethyl anthraquinone, bends anthraquinone, aminoanthraquinone, Anthraquinone, such as chloro anthraquinone, acetophenones, benzoin methyl ether, Benzoin ether, such as benzoin ethyl ether and benzoin phenyl ether, 2, 4, 6-trihalomethyl triazine, 1-hydroxy cyclohexyl phenyl ketone, 2-(o-chlorophenyl)-4, 5-diphenyl imidazole dimer, 2-(o-chlorophenyl)-4, 5-JI (m-methoxyphenyl) imidazole dimer, 2-(o-fluoro phenyl)-4, 5-diphenyl imidazole dimer, 2-(o-methoxyphenyl)-4, 5-diphenyl imidazole dimer, 2-(p-methoxyphenyl)-4, 5-diphenyl imidazole dimer, 2, a 4-JI (p-methoxyphenyl)-5-phenyl imidazole dimer, 2-(2, 4-dimethoxy phenyl)-4, 5-diphenyl imidazole dimer, etc., 2, 4, 5-thoria rell imidazole dimers, benzyl dimethyl ketal, 2-benzyl-2-dimethylamino -1 -(4-morpholino phenyl)- Butane-1-ON, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino-1-propanone, 2-hydroxy-2-methyl-1-phenyl-propane-1-ON, 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-ON, A phenanthrene quinone, 9, 10-phenanthrene quinone, a methyl benzoin, An acridine derivative and bis-acyl phosphine oxide, such as a benzoins [, such as an ethyl benzoin,], 9-phenyl acridine, 1, and 7-bis(9 and 9'-acridinyl) heptane, such mixture, etc. are mentioned.

[0030]

In addition to these initiators, an accelerator etc. can also be added. As these examples, p-dimethylamino ethyl benzoate, p-dimethylamino isoamyl benzoate, ethanolamine, diethanolamine, triethanolamine, etc. are mentioned.

[0031]

Moreover, to the photopolymer constituent of this invention, it is the purpose of sensibility and hardened material physical-properties adjustment, and it is also possible to add a polymerization nature monomer. As an example, polyethylene-glycol diacrylate (the number of ethylene is the thing of 2-14), Polyethylene glycol dimethacrylate (the number of ethylene is the thing of 2-14), Trimethylol propane diacrylate, trimethylol propane dimethacrylate, Trimethylolpropane triacrylate, trimethylolpropanetrimethacrylate, Trimethylol propane ethoxy thoria KURIRETO, trimethylol propane ethoxy trimethacrylate, Trimethylolpropane propoxy triacrylate, trimethylol propane propoxy trimethacrylate, Tetramethylolmethane triacrylate, tetramethylolmethane trimethacrylate, Tetramethylolmethane tetraacrylate, tetramethylolmethane tetra-methacrylate, Polypropylene-glycol diacrylate (the number of propylene radicals is the thing of 2-14), Polypropylene-glycol dimethacrylate (the number of propylene radicals is the thing of 2-14), Dipentaerythritol pentaacrylate, dipentaerythritol pentamethacrylate, Dipentaerythritol hexaacrylate, dipentaerythritol hexamethacrylate, Bisphenol A

polyoxyethylene diacrylate, bisphenol A polyoxyethylene dimethacrylate, Bisphenol A dioxy ethylene diacrylate, bisphenol A dioxy ethylene dimethacrylate, Bisphenol A trioxyethylene diacrylate, bisphenol A trioxyethylene dimethacrylate, Bisphenol A deca oxyethylene diacrylate, bisphenol A deca oxyethylene dimethacrylate, the compound (beta-hydroxyethyl acrylate --) which has polyvalent carboxylic acid (phthalic anhydride etc.), a hydroxyl group, and an ethylene nature partial saturation radical the alkyl ester (acrylic-acid methyl ester --) of an esterification object with beta-hydroxyethyl methacrylate etc., an acrylic acid, or a methacrylic acid methacrylic acid methylester, acrylic acid ethyl ester, ethyl methacrylate ester, acrylic-acid butylester, methacrylic-acid butylester, 2-ethylhexyl acrylate ester, 2-ethylhexyl methacrylate ester, etc. -- etc. -- it is mentioned.

[0032]

Furthermore, well-known things, such as polymerization inhibitor, a plasticizer, a pigment, a color, a surfactant, a defoaming agent, and a coupling agent, can be conventionally blended as other components if needed.

[0033]

Since the photopolymer constituent of above-mentioned this invention is high sensitivity also in the state of low concentration, it can form water gel by carrying out a photopolymerization reaction also as a low concentration water solution of 3% or less of solid content concentration.

[0034]

Moreover, the photopolymer constituent of this invention can mix various kinds of drug effect components which form a function, an enzyme, a fungus body, etc. In this case, the water gel which included various kinds of drug effect components, the enzyme, the fungus body, etc. can be formed by carrying out photo-curing of the photopolymer constituent containing various kinds of drug effect components, an enzyme, a fungus body, etc. Of course, after forming water gel from the photopolymer constituent of this invention, various kinds of drug effect components, an enzyme, a fungus body, etc. may be infiltrated.

[0035]

In addition, since patterning of the photopolymer constituent of this invention can be carried out like the usual resist constituent, it can also carry out patterning of various kinds of drug effect components which form a function, an enzyme, the fungus body, etc. with photolithography.

[0036]

[Embodiment of the Invention]

Although this invention is explained below based on an example, since it changes with the class of photopolymer constituent constituted using this photopolymer, and purposes of use, it is instantiation to the last and the range of this invention is not restricted.

[0037]

(Example 1)

After making a 75g methanol carry out the heating dissolution of the 10g (NIPPON SHOKUBAI [Co., Ltd.] make: AKUA rucksack AS-58 weight average molecular weight 800,000) of the polyacrylic acid, pyridine 1.1g was added as a catalyst for 4-hydroxy butyl acrylate glycidyl ether (Nippon Kasei Chemical [Co., Ltd.] make: 4HBAGE) 1.6g and promotion of a reaction, and it stirred in the 55-degree C water bath for 24 hours. Furthermore, while water bath temperature was raised to 90 degrees C and water was dropped, after distilling out a methanol, ion-exchange resin (Mitsubishi Chemical make-K-216 H) processing was performed, the pyridine was removed, and the water solution of the photopolymer (A) of 13% of nonvolatile matter concentration was obtained. It was 630 mgKOH/g when the solid content acid number of this photopolymer (A) was titrated in 0.1M water solution of NaOH. 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-ON (Ciba Specialty Chemicals make: IRGACURE-2959) 0.1g was added as a photopolymerization initiator to 100g of 13% water solutions of this photopolymer (A), and the target photopolymer constituent water solution was obtained.

[0038]

This photopolymer constituent water solution was diluted to the concentration of Table 1 with water, where it put each into the test tube and it is sealed, after the metal halide lamp UV irradiation machine of

illuminance 250 mW/cm² performed UV irradiation for 4 seconds, the test tube was uprighted, the plug was vacated, the iron ball with a weight of 5.5g was put on the oil level, and comparative evaluation of the hardenability was carried out by sedimentation and maintenance of an iron ball.

[0039]

[Table 1]

| 固形分濃度 | 2 % | 3 % | 4 % | 6 % | 8 % | 10 % |
|-------|-----|-----|-----|-----|-----|------|
| 鉄球状態 | 沈降 | 保持 | 保持 | 保持 | 保持 | 保持 |

[0040]

(Example 2)

The water solution of the photopolymer (A) compounded in the example 1 was neutralized by the sodium hydroxide, and the water solution of pH=6.0 and 10.4% of nonvolatile matter concentration was obtained. To 100g of this solution, 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-ON (Ciba Specialty Chemicals make: IRGACURE-2959) 0.08g was added as a photopolymerization initiator, and the photopolymer constituent water solution was obtained.

[0041]

This photopolymer constituent water solution was diluted to the concentration of Table 2 with water, and comparative evaluation of the hardenability was carried out by sedimentation and maintenance of an iron ball on the same conditions as an example 1.

[0042]

[Table 2]

| 固形分濃度 | 2 % | 3 % | 4 % | 6 % | 8 % | 10 % |
|-------|-----|-----|-----|-----|-----|------|
| 鉄球状態 | 沈降 | 保持 | 保持 | 保持 | 保持 | 保持 |

[0043]

(Example 1 of a comparison)

PVA-SbQ resin (Oriental composition industrial company make: SPP-H-13 polymerization degree 1700) was diluted to the concentration of Table 3 with water, and the same approach as an example 1 estimated hardenability.

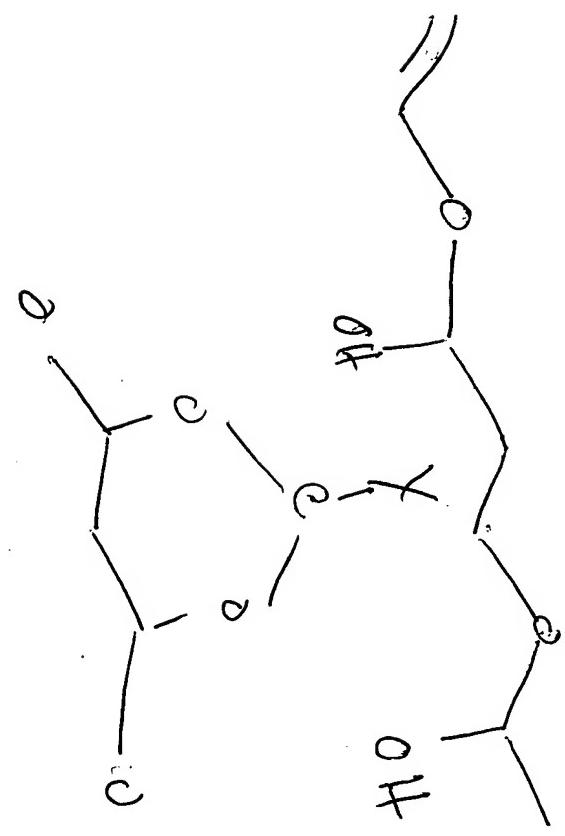
[0044]

[Table 3]

| 固形分濃度 | 2 % | 3 % | 4 % | 6 % | 8 % | 10 % |
|-------|-----|-----|-----|-----|-----|------|
| 鉄球状態 | 沈降 | 沈降 | 沈降 | 沈降 | 保持 | 保持 |

[0045]

As shown in Tables 1-3, in the examples 1 and 2, even if solid content concentration is 3% and a low



concentration water solution, it is firm and uniform water gel, and the iron ball was able to be held. On the other hand, in the example 1 of a comparison, unless it was a high-concentration water solution compared with 8% of solid content concentration, and an example, an iron ball was not able to be held. [0046]

[Effect of the Invention]

As explained above, since it excels in preservation stability, and it has the compatibility over various compounds, and mixed solubility and low concentration can also form firm and uniform water gel at very high speed, the photopolymer constituent of this invention is very useful.

[Translation done.]

